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### Use of Solubilized, Anionic Polyurethanes in Skin Care Compositions

### 5 BACKGROUND OF THE INVENTION

The present invention relates to the use of solubilized, anionic polyurethanes in skin care compositions.

Polyurethanes are known in the art as thickeners for compositions containing surface-active agents and for their use in hair fixative applications. United States Patent Nos. 5,626,840; 5,968,494; and 6,291,580 as well as European Patent Application 99102797.0 (Publication No. EP 0 937 541) all disclose polyurethanes with carboxylate functionality for hair fixative applications.

Polyurethanes are also known for other applications, including cosmetic compositions. However, such polyurethanes are typically formulated in the dispersed state. Polyurethane dispersions are easier to manufacture than solutions. However, dispersed polyurethanes may result in many undesirable properties when formulated in cosmetic formulations. Dispersed polyurethanes are not good film formers, and their use may result in greasy, harsh or uneven feel, long application times, shiny appearance, poor substantivity and/or grittiness.

Other polymers are commonly used in skin care formulas, such as polyacrylates and polymers prepared from alkenes. From a formulator's standpoint, those polymers suffer from the need to heat at elevated temperatures, optionally in the presence of neutralizing agents, to assist in solubilization.

Surprisingly, it has now been discovered that the use of anionic polyurethanes in a solubilized state contribute enhanced aesthetics to skin care compositions without the disadvantages of previously known compositions.

### SUMMARY OF THE INVENTION

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This patent pertains to the use of anionic polyurethanes in a solubilized state which contribute to enhanced aesthetics to skin care compositions.

### DETAILED DESCRIPTION OF THE INVENTION

This patent pertains to the use of anionic polyurethanes in a solubilized state contributing to enhanced aesthetics to skin care compositions.

Any anionic polyurethanes may be used in the skin care compositions of the present invention, including without limitation, those disclosed in United States Patent Nos. 5,626,840; 5,968,494; and 6,291,580 as well as European Patent Application 99102797.0 (Publication No. EP 0 937 541), hereby incorporated by reference. Particularly suitable are anionic polyurethanes, more particularly polyurethanes which incorporate 2,2-hydroxymethyl substituted carboxylic acid. In one embodiment, the polyurethane is limited by the proviso that it not contain a polycondensate of lactic acid.

The polyurethane may be used alone, or in combination with other polymers including, without limitation, acrylate and methacrylate polymers, as well as acrylamide/methacrylamide-based polymers, and polymers derived from other monomers such as maleic anhydride, maleates, butadiene, styrene and its derivatives, vinyl esters, isobutylene, maleimide and substituted maleimides, vinyl amides such as vinyl pyrrolidone and its derivatives, vinyl lactams such as polyvinyl caprolactam, itaconic acids and its esters, alkenes such as eicosene, zwitterionic monomers, cationic monomers such as acrylamidopropyltrimethylammonium chloride and vinylimidazolium chloride. Other combinations include polyesters,

polyethers, polyamides, polyesteramides, polyoxazolines, polyols, polyalkylene glycols, other urethane-containing polymers, hydrogels, silicones and silicone-containing copolymers, natural and modified polymers such as cellulose, starches, xanthan, shellac, alginates, guars and other natural and modified gums. A particularly suitable combination is the polyurethane in combination with acrylate and methacrylate polymers, particularly with a poly(meth)acrylate. Such combination may be in any form, including without limitation a simple mixture, a copolymer, or an interpenetrating polymer network.

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The polyurethane or polyurethane mixture is solubilized in a suitable solvent using techniques known in the art. Such solvents include without limitation alcohols such as methanol, ethanol, propanol, ethers, esters such as ethyl acetate and propyl acetate, diols such as ethylene glycol, polyols such as glycerol and sorbitol, amides, carbamates, sugars, substituted ethers such as dipropylene glycol dibutyl ether, and non protic polar solvents such as N-methyl pyrrolidone. An advantage of the present polyurethanes is that they do not require thermal energy or long stirring time for solubilization and they may be sold in a dissolved form (solution).

The solubilized polyurethane or polyurethane mixture is advantageous as it may be added directly to the skin care composition without the need for neutralization or may be sold in a neutralized form. In one embodiment of the present invention, the polyurethane is not neutralized.

The solubilized polyurethane or polyurethane mixture may be used in any skin care composition. Such skin care compositions are intended to include without limitation sunscreen and suntan compositions, after-sun compositions, hand and body moisturizers, face creams and lotions, skin tightening and firming compositions, and cleansing compositions, color cosmetics, and whitening compositions.

The solubilized polyurethane or polyurethane mixture is typically present in an amount of at least about 0.1%, more particularly at least about 0.2, most particularly at least about 0.5 and no more than about 15%, more particularly no more than about 10%, most particularly no more than about 5%, by weight of the skin care composition.

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Other additives commonly used in skin care compositions may be present in amounts known in the industry. Such additives include without limitation oils, waxes, acidifying or alkalinizing agents, preservatives, active agents, thickeners, emulsifiers, UV agents, emollients, fragrances, antioxidants, odor absorbents, defoamers, lightening agents, pigments, vitamins, botanicals, proteins, enzymes and coenzymes, and colors. In a particularly suitable embodiment, no plasticizer is used.

Yet other additives that can be present in the formulations which can provide therapeutic effects, such as in the treatment of dermatitis hypetiformis, warts, urticaria, hives, scars, keloids, scleroderma, lupus erythematosus, hirsutism, acne, pimples, athlete's foot, herpes, and other conditions as described in *Modern Pharmaceutics*, 3<sup>rd</sup> edition, ed. Gilbert Banker, Christopher Rhodes, Marcel Dekker, New York (1995). As used herein, therapeutic additives will be used to describe such additives.

The resultant skin care compositions have enhanced aesthetics due to the presence of the solubilized anionic polyurethane. Such enhancement may include reduction in greasiness, reduction in gloss, lighter feel, improved smoothness and increased adsorption. The polyurethanes also impart film-forming benefits of importance in moisturizing compositions and stabilizing benefits for colloidal or emulsified systems. Further, the solubilized polyurethane or polyurethane mixture are soluble in aqueous-based formulations and removable by using water or traditional cleansing systems such as soaps and body washes.

The enhanced skin care compositions are applied in the same manner as those known in the art.

### **EXAMPLES**

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The following examples are presented to further illustrate and explain the present invention and should not be taken as limiting in any regard. All percents used are on a weight/weight basis.

# Example 1 - Hand and Body Moisturizing Lotions

A. Polyurethane in the Aqueous Phase

<u>Ingredients</u>	INCI Designation	<u>% w/w</u>	<u>Supplier</u>
Phase A			
Carnation White Mineral Oil	Mineral Oil	10.00	Penreco
Estol 1517	Isopropyl Palmitate	6.00	Uniqema
Emersol 132	Stearic Acid T.P	2.00	Emery
Cetyl Alcohol	Cetyl Alcohol	1.00	
Ceralan	Lanolin Alcohol	0.50	Amerchol
Arlacel 165	Glyceryl Stearate/ PEG- 100 Stearate	3.50	Uniqema
DC 345	Fluid Cyclomethicone	1.00	Dow Corning
DC 556	Fluid Phenyl Trimethicone	1.00	Dow Corning
Vitamin E Acetate-C	Tocopheryl Acetate	1.00	Roche
Propylparaben	Propylparaben	0.10	

Substitute specification

Phase B	<u> </u>	T .	1
			<b></b>
Deionized Water	Water (Aqua)	65.74	
Triethanolamine (99%)	Triethanolamine	0.65	Dow
Carbopol Ultrez	Carbopol Ultrez	0.16	Noveon
Methylparaben	Methylparaben	0.15	
Trisodium EDTA	Trisodium EDTA	0.05	AKZO
Phase C			
Propylene Glycol	Propylene Glycol	3.00	
Polyurethane/Pol yacrylate <sup>1</sup>	Polyurethane (and) polyacrylate copolymer [proposed]	7.28	National Starch and Chemical Company
Phase D			
Germall II	Diazolidinyl Urea	0.15	Sutton Labs

<sup>&</sup>lt;sup>1</sup>Mixture of polyurethane and acrylates copolymer with polyurethane as the major component, 28% solids, 25% ethanol.

Phase B was combined and heated to 80°C. Phase A was combined and heated to 80°C. Phase A was then added to Phase B and mixed for 15 minutes. The mixture was cooled to 40°C. Phase C was combined and added to mixture A/B at 40°C, mixing thoroughly. Phase D was added to mixture A/B/C and mixed until uniform. The mixture was cooled to room temperature.

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B Polyurethane in the oil phase

D. Toryaroural	B. Polydretiane in the on phase			
<u>Ingredients</u>	INCI Designation	<u>% w/w</u>	<u>Supplier</u>	
Phase A				
Mineral Oil	Mineral Oil	10.00	Penreco	
Estol 1517	Isopropyl Palmitate	6.00	Uniqema	
Emersol 132	Stearic Acid T.P	2.00	Emery	
Cetyl Alcohol	Cetyl Alcohol	1.00		
Ceralan	Lanolin Alcohol	0.50	Amerchol	
Polyurethane/pol yacrylate <sup>1</sup>	Polyurethane (and) polyacrylate copolymer [proposed]	7.28	National Starch and Chemical Company	

Phase B			
Deionized Water	Water (Aqua)	69.05	
Triethanolamine (99%)	Triethanolamine	0.65	Dow
Carbopol Ultrez	Carbopol Ultrez	0.16	Noveon
Phase C			
Phenonip	Phemoxyethanol , Methylparaben, Butylparaben, Ethylparaben, Propylparaben	0.80	Nipa

<sup>&</sup>lt;sup>1</sup>Mixture of polyurethane and acrylates copolymer with polyurethane as the major component, 28% solids, 25% ethanol.

Phase B was combined and heated to 80°C. Phase A was combined and heated to 80°C. Phase A was added to Phase B and mixed for 15 minutes. Mixture A/B was cooled to 40°C. Phase C was added to mixture A/B at 40°C, mixing until uniform. The mixture was cooled to room temperature.

# 10 Example 2 - Skin tightening emulsion

<u>Ingredients</u>	INCI Designation	<u>% w/w</u>	Supplier
Phase A			
Emulgade SE	Glyceryl Stearate, Ethoxylated Cetearylachohol, Cetearyl alcohol, Cetyl palmate	7.00	Care Chem
Lipoval CO	Castor Oil	6.00	Chas Chem
Pristerene 4911	Stearic Acid	3.00	Uniquema
Prisorine 2040	Glyceryl Monoisostearate	2.00	Uniqema
Pricerene 9088	Glycerin	2.00	Uniqema
Fancol CB	Cocoa Butter	1.00	Fanning
Lipovol WGO	Wheat Germ Oil	1.00	Lipo
Propylparaben	Propylparaben	0.10	

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Phase B			
Deionized Water	Water (Aqua)	70.6	
Polyurethane/pol yacrylate <sup>1</sup>	Polyurethane (and) polyacrylate copolymer [proposed]	2.50	National Starch and Chemical Company
FLEXAN® 130 polymer	Sodium Polystyrene Sulfonate	2.50	National Starch and Chemical Company
STRUCTURE® SOLANACE polymeric thickener	Potato starch modified	2.00	National Starch and Chemical Company
Methylparaben	Methylparaben	0.15	
Phase C			
Germall II	Diazolidinyl Urea	0.15	

<sup>&</sup>lt;sup>1</sup>Mixture of polyurethane and acrylates copolymer with polyurethane as the major component, 28% solids, 25% ethanol.

Phase B was combined and heated to 80°C. Phase A has combined and heated to 80°C. Phase A was added to Phase B at 80°C and mixed for 15 minutes. The mixture was cooled to 40°C, and Phase C was added, mixing thoroughly. The mixture was cooled to room temperature.

# Example 3 – Moisturizing Face Cream A.

Ingredients	_A.			
Emulgade SE  Glyceryl Stearate, Ethoxylated Cetearylachohol, Cetyl palmate  Lipoval CO Castor Oil Pristerene 4911 Stearic Acid Oglyceryl Monoisostearate  Pricerene 9088 Glycerin Fancol CB Cocoa Butter Lipovol WGO Propylparaben  Propylparaben  Propylparaben  Propylparaben  Polyurethane/pol yacrylate¹ Copolymer [proposed]  Carbopol 940  Carbomer  Methylparaben  Methylparaben  Polyurethane/pol yacrylate  Carbomar  Triethanolamine (99%)  Methylparaben  Methylparaben  Carsonol, Cetyl palmate  A.00 Chas Chem Chas Chem Uniquema  Lipoud Uniqema  Lipoud Uniqema  Lipoud Uniqema  Fanning Lipoud Lipo  Valiquema  Lipoud Lipo  Valiquema  Lipoud  Valiquema  Valiquema  Valiquema  Lipoud  Valiquema  Lipoud  Valiquema  Lipoud  Valiquema  Lipoud  Valiquema  Valiquema		INCI Designation	<u>% w/w</u>	Supplier
Stearate, Ethoxylated Cetearylachohol, Cetyl palmate  Lipoval CO Castor Oil 6.00 Chas Chem  Pristerene 4911 Stearic Acid 3.00 Uniquema  Prisorine 2040 Glyceryl 2.00 Uniqema  Pricerene 9088 Glycerin 2.00 Uniqema  Fancol CB Cocoa Butter 1.00 Fanning  Lipovol WGO Wheat Germ Oil 1.00 Lipo  Propylparaben Propylparaben 0.10  Phase B  Deionized Water Water (Aqua) 72.20  Polyurethane/pol yacrylate copolymer [proposed]  Carbopol 940 Carbomer 0.20 Noveon  Triethanolamine (99%)  Methylparaben Methylparaben 0.15  Phase C	Phase A			
Pristerene 4911 Stearic Acid 3.00 Uniquema Prisorine 2040 Glyceryl 2.00 Uniqema  Pricerene 9088 Glycerin 2.00 Uniqema Fancol CB Cocoa Butter 1.00 Fanning Lipovol WGO Wheat Germ Oil 1.00 Lipo Propylparaben Propylparaben 0.10  Phase B Deionized Water Water (Aqua) 72.20 Polyurethane/pol yacrylate¹ (and) polyacrylate copolymer [proposed] Carbopol 940 Carbomer 0.20 Noveon  Triethanolamine (99%) Methylparaben Methylparaben 0.15 Phase C		Stearate, Ethoxylated Cetearylachohol, Cetearyl alcohol, Cetyl palmate		
Prisorine 2040  Glyceryl Monoisostearate  Pricerene 9088  Glycerin  Fancol CB Cocoa Butter Lipovol WGO Vheat Germ Oil Propylparaben  Propylparaben  Propylparaben  Polyurethane/pol yacrylate¹ Copolymer [proposed]  Carbopol 940  Carbomer  Pricerene 9088  Glycerin  2.00 Uniqema Fanning Lipo Fanning Lipo  Fanning Lipo  Fanning Lipo  National Starch and Chemical Company  Company  Dow  Polyurethane (and) polyacrylate copolymer [proposed]  Carbopol 940  Triethanolamine (99%)  Methylparaben  Methylparaben  Methylparaben  Methylparaben  Methylparaben  Noveon  Dow	Lipoval CO	Castor Oil	6.00	Chas Chem
Pricerene 9088 Glycerin 2.00 Uniqema Fancol CB Cocoa Butter 1.00 Fanning Lipovol WGO Wheat Germ Oil 1.00 Lipo Propylparaben Propylparaben 0.10  Phase B  Deionized Water Polyurethane/pol yacrylate¹ (and) polyacrylate copolymer [proposed]  Carbopol 940 Carbomer 0.20 Noveon  Triethanolamine (99%)  Methylparaben Methylparaben 0.15  Phase C	Pristerene 4911	Stearic Acid	3.00	Uniquema
Fancol CB Lipovol WGO Wheat Germ Oil Propylparaben Propylparaben Propylparaben  Deionized Water Polyurethane/pol yacrylate¹ Carbopol 940  Carbomer  Triethanolamine (99%) Methylparaben  Cocoa Butter 1.00 Fanning Lipo Fanning Lipo Lipo  Fanning Lipo Lipo  Fanning Lipo Lipo  National Starch and Chemical Company  Dow  Noveon  Dow  Dow  Dow  Dow  Methylparaben  Methylparaben  Methylparaben  Dos  Dow  Dow  Dow  Dow  Dow  Dow  Dow	Prisorine 2040		2.00	Uniqema
Fancol CB Cocoa Butter 1.00 Fanning Lipovol WGO Wheat Germ Oil 1.00 Lipo  Propylparaben Propylparaben 0.10  Phase B Deionized Water Water (Aqua) 72.20  Polyurethane/pol yacrylate¹ (and) polyacrylate copolymer [proposed]  Carbopol 940 Carbomer 0.20 Noveon  Triethanolamine (99%)  Methylparaben Methylparaben 0.15  Phase C	Pricerene 9088	Glycerin	2.00	Uniqema
Propylparaben Propylparaben 0.10  Phase B  Deionized Water Water (Aqua) 72.20  Polyurethane/pol yacrylate¹ (and) polyacrylate copolymer [proposed]  Carbopol 940 Carbomer 0.20 Noveon  Triethanolamine (99%)  Methylparaben Methylparaben 0.15  Phase C	Fancol CB	Cocoa Butter	1.00	Fanning
Phase B  Deionized Water Water (Aqua) 72.20  Polyurethane/pol yacrylate¹ (and) polyacrylate copolymer [proposed]  Carbopol 940 Carbomer 0.20 Noveon  Triethanolamine (99%)  Methylparaben Methylparaben 0.15  Phase C	Lipovol WGO	Wheat Germ Oil	1.00	Lipo
Deionized Water Water (Aqua) 72.20  Polyurethane/pol yacrylate¹ Polyurethane (and) polyacrylate copolymer [proposed]  Carbopol 940 Carbomer 0.20 Noveon  Triethanolamine (99%)  Methylparaben Methylparaben 0.15  Phase C	Propylparaben	Propylparaben	0.10	
Polyurethane/pol yacrylate¹	Phase B			
yacrylate¹ (and) polyacrylate copolymer [proposed]  Carbopol 940  Carbomer  O.20  Noveon  Triethanolamine (99%)  Methylparaben  Methylparaben  Methylparaben  Methylparaben  Methylparaben  Methylparaben  Methylparaben  O.20  Dow  O.20  Phase C	Deionized Water	Water (Aqua)	72.20	·
Triethanolamine (99%)  Methylparaben Methylparaben 0.15  Phase C	Polyurethane/pol yacrylate <sup>1</sup>	(and) polyacrylate copolymer		and Chemical
(99%)  Methylparaben Methylparaben 0.15  Phase C	Carbopol 940	Carbomer	0.20	Noveon
Phase C	(99%)	Triethanolamine	0.20	Dow
Phase C	Methylparaben	Methylparaben	0.15	
Germall II Diazolidinyl Urea 0.15				
	Germall II	Diazolidinyl Urea	0.15	

<sup>&</sup>lt;sup>1</sup>Mixture of polyurethane and acrylates copolymer with polyurethane as the major component, 28% solids, 25% ethanol.

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Phase B was combined and heated to 80°C. Phase A was combined and heated to 80°C. Phase A was added to Phase B at 80°C and mixed for 15 minutes. The mixture was cooled to 40°C, and Phase C was added, mixing thoroughly. The mixture was cooled to room temperature.

B. Example 3A was repeated except that FLEXAN® 130 polymer was partially substituted for the polyurethane/polyacrylate.

# Example 4 - Moisturizing Face Lotion

 $5\overline{A}$ 

Ingredient	INCI Designation	<u>%w/w</u>	Supplier
Phase A			
Arlacel 165	Glyceryl Stearate, PEG-100 Stearate	7.00	Uniqema
Finsolv TN	C12-15 Alkyl Benzoate	6.00	Finetex
Cetyl Alcohol	Cetyl Alcohol	5.00	
Vitamin E Acetate-C	Tocopheryl Acetate	1.00	Roche Vitamins
dl-alpha Tocopheryl Acetate		1.00	Roche Vitamins
DC 345	Fluid Cyclomethicone	1.00	Dow Corning
DC 556	Fluid Phenyl Trimethicone	1.00	Dow Corning
Phase B			
Deionized Water	Water (Aqua)	74.65	
Carbopol 940	Carbomer	0.20	Noveon
Triethanolamine (99%)	Triethanolamine	0.20	Dow
Versene 100	Tetrasodium EDTA	0.15	Dow Chemical
Phase C			
Polyurethane/pol yacetate	Polyurethane (and) polyacrylate copolymer [proposed]	2.00	National Starch and Chemical Company
Phenonip	Phenoxyethanol, Methylparaben, Butylparaben, Ethylparaben, Propylparaben	0.80	Nipa

<sup>&</sup>lt;sup>1</sup>Mixture of polyurethane and acrylates copolymer with polyurethane as the major component, 28% solids, 25% ethanol.

Phase B was combined and heated to 80°C. Phase A was combined and heated to 80°C. Phase A was added to Phase B at 80°C and mixed for 15 minutes. The mixture was cooled to 40°C, to which Phase C was added, and mixed until uniform. The mixture was cooled to room temperature.

Example 5 – Sunscreen Emulsion

INCI Designation	<u>%w/w</u>	<u>Supplier</u>
C12-15 Alkyl	6.00	Finetex
		<u></u>
Octyl Salicylate	5.00	H&R
	7.50	H&R
	4.00	H&R
	1.00	
	1.60	Roche
	2.00	Goldschmidt
	3.00	Goldschilliat
	0.60	Croda
	0.00	Cioda
	3.00	Dow Corning
Difficulticorie	3.00	Dow Conning
Tocopheryl	0.10	Roche
		1.100.110
Water (Aqua)	20.00	
Acrylates/C10-	0.18	Noveon
30 Álkyl Acrylate		
Crosspolymer		
Tetrasodium	0.15	Dow Chemical
EDTA		
	C12-15 Alkyl Benzoate Octyl Salicylate  Ethylhexyl Methoxycinnama te Benzophenone-3 (Oxybenzone) Butyl Methoxydibenzo ylmethane (Avobenzone) Polyglyceryl-3 Methylglucose Distearate C18-36 Acid Glycol Ester Dimethicone  Tocopheryl Acetate  Water (Aqua) Acrylates/C10- 30 Alkyl Acrylate Crosspolymer Tetrasodium	C12-15 Alkyl Benzoate Octyl Salicylate  Ethylhexyl Methoxycinnama te  Benzophenone-3 (Oxybenzone) Butyl Methoxydibenzo ylmethane (Avobenzone) Polyglyceryl-3 Methylglucose Distearate C18-36 Acid Glycol Ester Dimethicone  Tocopheryl Acetate  Water (Aqua) Acrylates/C10- 30 Alkyl Acrylate Crosspolymer Tetrasodium  0.15

Phase C			
1,4 Butanediol	Butylene Glycol	4.00	BASF
TEA 99%	Triethanolamine	0.18	Union Carbide
Deionized Water	Water (Aqua)	41.11	
Polyurethane/pol yacrylate	Polyurethane (and) polyacrylate copolymer [proposed]	7.28 (2.0 % dry basis)	National Starch and Chemical Company
Phase D			
TEA 99%	Triethanolamine	0.08	Union Carbide
Phase E			
Phenonip	Phenoxyethanol, Methylparaben, Butylparaben, Ethylparaben, Propylparaben	0.80	Nipa

<sup>1</sup>Mixture of polyurethane and acrylates copolymer with polyurethane as the major component, 28% solids, 25% ethanol.

- The first three ingredients of Phase A were combined and mixed well. Neo Heliopan BB was added and mixed at room temperature for 10 minutes. While mixing, the mixture was heated to 80°C. Parsol 1789 was added and mixed for 5 more minutes while keeping temperature at 80°C. Tego Care 450 was added and mixed 2-3 minutes. Syncrowax ERL-C was added and mixed for another 2-3 minutes. The remaining ingredients of Phase A are added and mixed, keeping the temperature of Phase A at 80°C. In a separate vessel, Carbopol EDT2020 was sifted in room temperature deionized water and mixed while heating to 75°-80°C. Versene 100 was added when Carbopol EDT2020 was completely dispersed.
- Butylene Glycol and TEA were premixed and the polyurethane/polyacrylate was added. The deionized water of Phase C was heated to 85°C then added to the other components of phase C at 85°C. Phase C was mixed for 5 minutes while keeping temperature at 80-85 C.

Phase A was slowly added to Phase B. Phase D was then added to mixture A/B until a pH of 6.5-6.6 is reached and mixed well. High shear mixing was applied and Phase C was added to mixture A/B/D at a temperature of 80-85°C. Phase E was added at a temperature of no more than 55°C. While cooling to 30°C, moderate mixing was applied. The mixture was then homogenized (~ 9,000 rpm) at 30°C for 3 - 5 minutes. The water loss was calculated and added back in to the mixture.

- B. Example 5A was repeated except that the amount of polyurethane/polyacrylate used was 3.64%w/w (1.0% on a dry weight basis) and water was added to make up the weight.
- C. Example 5A was repeated except that 2.00%w/w DERMACRYL® polymer (commercially available from National Starch and Chemical
   Company) was added in Phase C and the polyurethane/polyacrylate was not used.

A subjective sensory panel (8 panelists) compared Samples 5A and 5C with the following results shown in Table 1:

Table 1

Sample	Example 5A	Example 5C
Smooth/soft	5/8	3/8
Greasy	1/8	7/8
Quick absorption	7/8	1/8
Tacky	0/8	8/8
Drag	2/8	6/8
Gloss	1/8	7/8
Light Feel	4/8	4/8
After feel	5/8	3/8

Substitute specification

Table 1 shows that the polyurethane/polyacrylate sample is significantly less greasy, less tacky, less shiny and is more quickly absorbed than the comparative example.

- 5 D. Example 5A was repeated except that the polyurethane/polyacrylate was omitted and in Phase C, 0.63% w/w TEA was used. Sample 5A provided improved afterfeel after a gentle water rinse.
- Samples D (control), A (2% polyurethane acrylate, dry basis), and C (2% Dermacryl, dry basis) were evaluated for in-vitro SPF efficiency. The control was found to confer a SPF of 36, as compared to 53 for sample A and 65 for sample C, demonstrating the film-forming behavior of solution polyurethanes.

# Example 6 – Sunscreen Emulsions A.

Ingredient	INCI Designation	%w/w
Phase A	THE POOL HEADER	70070
Water	Water, deionized	75.70
Versene 100	Tetrasodium EDTA	0.20
Princerine 9088	Glycerine	2.00
Carbomer	Carbopol 940	0.20
Phase B		
Hall Brite TQ	Diethylhexyl naphthalate	3.10
Neo Heliopan AV	Octyl Methoxycinnama te	3.10
Neo Heliopan OS	Octyl Salicylate	3.50
Parsol 1789	Butyl Methoxydi- benzoylmethane	2.00
Dow 193	Dimethicone Copolymer	1.00
Dow 200/100cps	Dimethicone	1.00
Brij 721	Steareth-21	0.80
Brij 72	Steareth-2	1.00
Arlacel 165	Glyceryl Stearate (and) PEG-100 Stearate	1.20
Phenonip	Phenoxyethanol, methylparaben, ethylparaben, propylparaben, butylparaben	1.00
Phase C		
Water	Water	0.00
TEA (99%)	Triethanolamine	0.20
Phase D		
Polyurethane (and) polyacrylate copolymer [proposed]	Polyurethane/pol yacrylate	4.00

Mixture of polyurethane and acrylates copolymer with polyurethane as the major component, 28% solids, 25% ethanol.

Substitute specification

Water, Tetrasodium EDTA and Glycerin of Phase A were combined at room temperature. Carbomer was slowly sprinkled onto the surface while stirring. After incorporating all the Carbomer, Phase A was heated to 80°C. Phase B was prepared separately, heated to 80°C and stirred until uniform.

- 5 Phase B was slowly added to Phase A with mixing. When the mixture appeared uniform, Phase C was added with mixing. After achieving uniformity again, the heat was turned off and mixing was switched to sweep. Sweep mixing was continued throughout cool-down. Phase D was added with stirring at 45°C. Water was added to make up for loss during heating and stirred to room temperature.
  - B. Example 6A was repeated except that water was substituted for the polyurethane/polyacrylate.
- Both samples produced a smooth, rich, white-colored emulsion. The samples were tested for SPF and water resistance using the following methodology.

#### Instrumentation:

20 A Labsphere UV1000S Ultraviolet Transmittance Analyzer was used to determine the absorbence spectra of the samples.

#### Substrate:

Vitro-Skin® - the skin was hydrated prior to use. Pieces of the Vitro-Skin® were cut to fit the slide mounts being used. A small hydration chamber was used. Approximately 200 ml of hydrating solution (30% glycerin in distilled water) were added to the chamber. The chamber was sealed and kept at a temperature of approximately 23°C for sixteen (16) hours. This provided the recommended humidity atmosphere for hydration of the Vitro-

Skin<sup>®</sup>. After Sixteen (16) hours, the skin was ready for use. Test materials were applied to the rough side of the Vitro-Skin<sup>®</sup>.

Five samples of substrate were used for each sample. One reference sample was also be prepared.

The substrate was placed on a balance and a 2 mg/cm<sup>2</sup> portion of the sample was applied using a syringe with a fine blunt needle. The substrate was removed from the balance and transferred to a foam block to simulate the flexibility of human dermis. The sample was distributed on the substrate by dotting the sunscreen on and noting the weight. The sunscreen-coated substrate was removed from the balance and spread evenly over the site using a fingercot for 20-30 strokes (approximately 20 seconds).

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After product application, the samples were allowed to dry for at least 15 minutes to let the emulsion break down. A blank (no sunscreen applied) substrate will serve as the reference untreated control.

### 20 Measurements:

Measurements were performed using the Labsphere UV-1000S Ultraviolet Transmittance Analyzer. A baseline scan was performed using the reference sample. A second scan of the reference sample was run. The results demonstrated a flat baseline at  $100\% \pm 0.5\%$ .

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Measurements for the sunscreen-substrate were then performed. Five measurements per sample were performed at various spots on the sample to ensure proper spreading of the test material.

### **WATER-RESISTANT**

**METHODOLOGY:** The Vitro-Skin<sup>®</sup> was immersed in a water bath for forty (40) minutes. After the dry time, the sunscreen-substrate preparation was insulted with a full spectrum UV dose corresponding to 1 MED times 1/3 the test material SPF value. It was calculated as follows:

UV Dose = 
$$\frac{SPF}{3}$$
 x 1 J/cm<sup>2</sup>

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### **VERY WATER-RESISTANT**

**METHODOLOGY:** The Vitro-Skin® was immersed in a water bath for eighty (80) minutes. After the dry time, the sunscreen-substrate preparation was insulted with a full spectrum UV dose corresponding to 1 MED times 1/3 the test material SPF value. It was calculated as follows:

UV Dose = 
$$\frac{SPF}{3}$$
 x 1 J/cm<sup>2</sup>

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Table 2

Polymer	Level - solids	Mean SPF	WR* SPF	VWR* SPF
Sample 6A	1	29.47	10.25	9.87
Sample 6B	0	26.07	1.78	

WR\* SPF - water resistant SPF, 40 min immersion VWR\* SPF - very water resistant SPF, 80 min immersion

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As can be seen from Table 2, the use of the polyurethane/polyacrylate added SPF protection as well as water resistance.

### Example 7 - Water Resistant Sunscreen

5	<u>Ingredient</u>	Amount (%w/w)
	Phase A	
	SDA-40 (Ethanol)	71.50
	Polyurethane	8.00 (2.0% solids)
	Phase B	,
10	C <sub>12-15</sub> Alkyl Benzoate	7.50
	Octyl Methoxycinnamate	5.00
	Octyl Salicylate	5.00
	Butyl Methoxydibenzoylmethane	3.00

15 Phase B ingredients were combined and heated to 75°C while mixing. The mixture was cooled to room temperature and premixed Phase A was added.

### 20 <u>Example 8 – Sunscreen with emulsified Polyurethane</u>

	<u>Ingredient</u>	<u>Amount (%w/w)</u>
	Phase A	
	Octyl Methoxycinnamate	7.50
25	Octyl Salicylate	5.00
	Isopropyl Palmitate	5.00
	Polyurethane	8.00 (2.0% solids)
	Phase B	,
	D.I.Water	73.50
30	Preservatives	1.00

Phase A ingredients were premixed. Phase B ingredients were premixed and slowly added to Phase A while homogenizing. A white, thin emulsion formed.

# Example 9 - Moisturizing Lotion

	Ingredient	Amount (%w/w)
E	Phase A:	25.00
5	C12-15 Alkyl Benzoate	25.00
	Polyurethane	6.70 (1.675% solids)
	Phase B	
	D.I. Water	68.30
	Preservatives	1.00

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Phase A ingredients were mixed well. Phase B ingredients were mixed and slowly added to Phase A. The mixture was homogenized.